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CLAIMS**[Claim(s)]**

[Claim 1] In a cross linked polyolefin pipe which consists of a copolymer of ethylene and alpha olefin whose carbon number is four or more, In a melt flow rate, density for 0.1-95g/10 minutes 0.850 - 0.970 g/cm³, [this copolymer] Q value (Mw/Mn) is less than 3.0, and carry out the graft of the vinyl silane compound to this copolymer under existence of a radical generator, and it is considered as modified resin, A cross linked polyolefin pipe carrying out the dew of this modified resin into water atmosphere under existence of a silanol condensation catalyst, and making not less than 65% of a gel fraction construct a bridge.

[Claim 2] In a cross linked polyolefin pipe which consists of a copolymer of ethylene and alpha olefin whose carbon number is four or more, In a melt flow rate, density for 0.1-95g/10 minutes 0.850 - 0.970 g/cm³, [this copolymer] A process of Q value (Mw/Mn) being less than 3.0, and making a vinyl silane compound this copolymer with modified resin under existence of a radical generator, A cross linked polyolefin pipe adding a silanol condensation catalyst with a single making machine, carrying out dew into water atmosphere after that, and making not less than 65% of a gel fraction construct a bridge.

[Claim 3] Claim 1 thru/or the cross linked polyolefin pipe according to claim 2 with which a copolymer of ethylene and alpha olefin is manufactured using a single site catalyst.

[Claim 4] Claim 1 thru/or the cross linked polyolefin pipe according to claim 2 whose vinyl silane compound is an ethylene nature unsaturation silane compound expressed with the following general formula [I].

[Formula 1]

(In general formula [I], R¹ is an ethylene nature unsaturation hydrocarbon group or a hydrocarbon oxy group, R² aliphatic series saturation hydrocarbon group and Y are the organic groups which can be hydrolyzed, and n is 0-2)

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to a cross linked polyolefin pipe. It is related with the outstanding endurance and the cross linked polyolefin pipe which demonstrates creep performance over a long period of time, and is especially used as the conduit tube, the protective tube of the cable for communication, a gas pipe, feed water and a hot-water pipe, a lead pipe of the heating fluid of a floor heater, etc. in more detail.

[0002]

[Description of the Prior Art] It is common knowledge to improve physical properties, such as heat resistance, creep resistance, environmental-stress-cracking-resistance nature (ESC), and chemical resistance, by making polyethylene construct a bridge conventionally. In order to continue at a long period of time and to demonstrate the creep performance outstanding with these cross-linked polyethylene pipe, it is made good for a melt flow rate (MFR) to use the resin which carried out the graft of the vinylsilane to low namely, polyethylene with a large molecular weight, and denaturalized.

[0003] However, probably in order for the chains of an ultrahigh-molecular-weight portion to construct a bridge in the modified resin having contained the polyethylene molecule with a large molecular weight, the motor load of a making machine becomes large at the time of cross-linked polyethylene pipe manufacture, and as a result, power consumption becomes large, and it becomes a high cost, and is not desirable. Although there is a method of making melting temperature of modified resin high and manufacturing a pipe as a method of on the other hand preventing the motor load of a making machine from becoming large, since this method promotes generating of a glow of modified resin and reduces the value as the long-term creep performance and the product of a pipe, it is not preferred.

[0004]

[Problem(s) to be Solved by the Invention] As a result of repeating research wholeheartedly in view of the above-mentioned situation, this invention persons vinylsilane as a graft and a raw material to denature. The motor load of the making machine at the time of manufacture does not become large, but the cross linked polyolefin pipe which selected the copolymer of specific ethylene and alpha olefins and was made to construct a bridge by a specific method comes to complete this invention based on the knowledge which continues at a long period of time and maintains the creep performance outstanding moreover.

[0005] The purpose of this invention is as follows. 1. Provide the cross linked polyolefin pipe with which the motor load of a making machine does not become large at the time of manufacture. 2. Provide the cross linked polyolefin pipe which does not produce generating of a glow of raw resin at the time of manufacture. 3. Provide the cross linked polyolefin pipe which continues at a long period of time and maintains the outstanding creep performance.

[0006]

[Means for Solving the Problem] In a cross linked polyolefin pipe which consists of a copolymer of ethylene and alpha olefin whose carbon number is four or more in this invention in order to solve an aforementioned problem, In a melt flow rate, density for 0.1-95g/10 minutes 0.850 - 0.970

g/cm^3 , [this copolymer] Q value (Mw/Mn) is less than 3.0, and carry out the graft of the vinyl silane compound to this copolymer under existence of a radical generator, and it is considered as modified resin. This modified resin is put into water atmosphere under existence of a silanol condensation catalyst, and a cross linked polyolefin pipe making not less than 65% of a gel fraction construct a bridge is provided.

[0007]In a cross linked polyolefin pipe which consists of a copolymer of ethylene and alpha olefin whose carbon number is four or more further in this invention. In a melt flow rate, density for 0.1-95g/10 minutes $0.850 - 0.970 \text{ g}/\text{cm}^3$. [this copolymer] A process of Q value (Mw/Mn) being less than 3.0, and making a vinyl silane compound this copolymer with modified resin under existence of a radical generator. A silanol condensation catalyst is added with a single making machine, dew is carried out into water atmosphere after that, and a cross linked polyolefin pipe making not less than 65% of a gel fraction construct a bridge is provided.

[0008]

[Embodiment of the Invention.] Hereafter, this invention is explained in detail. In this invention, the polyolefine refers to the copolymer of ethylene and the alpha olefins whose carbon number is four or more. As alpha olefins whose carbon number is four or more, 1-butene, a 2-methyl-1-butene, 1-pentene, 2-methyl-1-pentene, 1-hexene, a 2,2-dimethyl-1-butene, a 2-methyl-1-hexene, 4-methyl-1-pentene, 1-heptene, a 2-methyl-1-hexene, A 3-methyl-1-hexene, 2,2-dimethyl-1-pentene, 3,3-dimethyl-1-pentene, 2,3-dimethyl-1-pentene, 3-ethyl-1-pentene, a 2,2,3-trimethyl-1-butene, 1-octene, 2,2,4-trimethyl-1-octene, etc. are mentioned.

[0009]The above-mentioned copolymer can be manufactured using a metallocene catalyst. Generally the designation of the catalyst of the structure which sandwiched the unsaturated compound of a pi electron system for the transition metal is carried out, the structure is indicated in the international publication W091 No. -04257 gazette, and bis(cyclopentadienyl) metallic compounds of a metallocene catalyst are typical. As a metallocene catalyst, the compound in which 1, two or more cyclopentadienyl rings, or the analog of those exists in tetravalent transition metals, such as titanium, a zirconium, nickel, palladium, hafnium, and platinum, as ligand (ligand) is specifically mentioned.

[0010]The metallocene catalyst which can be preferably used for manufacture of the above-mentioned copolymer is a nonelectrolyte complex, two cyclopentadienyl rings have regular pentagon structure, and faces in parallel mutually, and presents the spacial configuration which a metal atom is inserted in the middle and consists of a molecule of sandwich structure. The ethylene and alpha olefin of a raw material of a copolymer, Since it cannot contact, but metal and a monomer will always contact from a fixed direction and stereospecific polymerization happens from the direction blocked in three dimensions by the substituent combined with the five membered ring combined with the metal atom. A molecular weight, branching structure, and a crystal structure become fixed, and the olefin system copolymer which a catalyst is called a single site catalyst and obtained has them. [preferred]

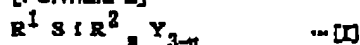
[0011]Restriction in particular does not have a manufacturing method of the above-mentioned copolymer, and it is good in both a solution polymerization method gas phase polymerization process a suspension polymerization method a mass polymerization method, etc.

[0012]In order to obtain the cross linked polyolefin pipe concerning this invention according to this invention persons' experiment, the melt flow rate (MFR.) which measured the above-mentioned copolymer based on JIS K6922-2 The conditions of the temperature of 190 ** and 2.16 kg of load 0.1-95g/range for 10 minutes, The density measured based on JIS K6922-2 was found by being the range of $0.850-0.970 \text{ g}/\text{cm}^3$, and that molecular-weight-distribution Q value [weight-average-molecular-weight (Mw) / number average molecular weight (Mn)] is [less than 3.0 thing] further suitable.

[0013]The cross linked polyolefin pipe concerning this invention carries out the graft of the vinyl silane compound to the above-mentioned olefine copolymer under existence of a radical generator, is used as modified resin, and makes this modified resin construct a bridge under existence of a silanol condensation catalyst. As a vinyl silane compound, what is expressed with the following general formula [] is mentioned.

[0014]

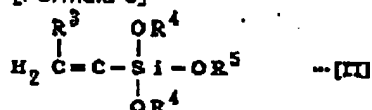
[Formula 2]



[0015] In general formula [I], R^1 is an ethylene nature unsaturation hydrocarbon group or a hydrocarbon oxy group, and has radical reactivity. As an example of such a basis, a vinyl group, an allyl group, a butenyl group, gamma-(meta) acryloxypropyl group, etc. are mentioned. R^2 is an aliphatic series saturation hydrocarbon group, and a methyl group, an ethyl group, a propyl group, a decyl group, etc. are mentioned as an example. Y expresses the organic group which can be hydrolyzed and a methoxy group, an ethoxy basis, a formyloxy group, an acetoxy group, a propionyloxy group, an arylamino group, etc. are mentioned as an example. n is 0, 1, or 2. Especially a desirable thing is a compound expressed with the following general formula [II] especially.

[0016]

[Formula 3]



[0017] As for R^3 , in general formula [II], a with a carbon number of four or less straight chain or a branched alkyl group, and R^5 of H or CH_3 , and R^4 are a with a carbon number of four or less straight chain, a branched alkyl group, or a phenyl group. Specifically, vinyltrimetoxysilane, vinyltriethoxysilane, a vinyl tripropoxy silane, etc. are mentioned.

[0018] When denaturing an olefine copolymer, the quantity of the vinyl silane compound made to exist in the system of reaction to denature is determined by the degree of cross linking of the resin pipe made into the purpose, the reaction condition (temperature, time), etc., but, it is chosen from a viewpoint of economical efficiency and the ease of the handling under reaction front and reaction in the range of 0.1 to 15 weight section to polyolefin copolymer 100 weight section. If there is too little this quantity, a graft rate will be low and sufficient degree of cross linking will not be obtained. If too large, the resin pipe of mold goods may serve as an appearance defect under the influence of a conversely unreacted vinyl silane compound, etc., and it is not desirable. The range with a preferred quantity of a vinyl silane compound is 0.3 to 10 weight section, and especially a desirable thing is 0.5 to 7 weight section.

[0019] As for a radical generator, it is preferred to choose from compounds which can generate an uncombined radical and have the half-life for less than 6 minutes at grafting reaction temperature under grafting reaction conditions. A compound which has the half-life for less than 1 minute at grafting reaction temperature is more preferred. All compounds indicated to JP,48-1711,B can use these radical generators. Specifically, azo compounds, such as organic peroxide, such as benzoyl peroxide, dicumyl peroxide, di-t-butyl peroxide, and t-butyloxy 2-ethylhexanoate, azobisisobutyronitrile, and methyl azobisisobutyrate, are mentioned.

[0020] When carrying out the grafting reaction of the vinyl silane compound to an olefine copolymer, quantity of a radical generator made to exist in a grafting reaction system is chosen in the range of 0.001 to 5 weight section to olefine copolymer 100 weight section. If there are too many amounts of grafts of a vinyl silane compound conversely few when there is too little quantity of a radical generator made to exist, crosslinking reaction which is not made into the purpose depended on a radical generator may advance, and it may become causes, such as aggravation etc. of appearance of a resin pipe which are the poor flowing characteristic and mold goods, and is not desirable. It is the range of 0.01 to 2.0 weight section more preferably.

[0021] A method of making carry out the graft of the vinyl silane compound to an olefine copolymer, and using as modified resin can be based on a method indicated in publications, such as JP,48-1711,B, JP,59-36115,A, and JP,55-9811,A, and can be manufactured easily.

[0022] In order to obtain a cross linked polyolefin pipe concerning this invention, the above-

mentioned modified resin is made to construct a bridge under existence of a silanol condensation catalyst. As a silanol condensation catalyst, metal carboxylate, such as tin, zinc, iron, lead, and cobalt, titanate and an organic metallic compound of chelate compound, an organic base, inorganic acid, organic acid, etc. are mentioned. Specifically Dibutyltin dilaurate, dibutyltin diacetate, a dioctyl tin JIRAU rate, The first tin of acetic acid, the first tin of caprylic acid, lead naphthenate, cobalt naphthenate, tetrabutyl titanate ester, titanate acid tetranonyl ester, dibutyl amine, hexylamine, pyridine, sulfuric acid, chloride, toluenesulfonic acid, acetic acid, stearic acid, maleic acid, etc. are mentioned.

[0023] When making said modified resin construct a bridge, in order to make a silanol condensation catalyst exist in a crosslinking reaction system, (a) How to blend as a masterbatch which carried out melt kneading of the silanol condensation catalyst to polyolefine a priori, (b) A method of blending a silanol condensation catalyst with modified resin directly as it is at the time of manufacture, a method of applying or impregnating with a pipe made of modified resin by using the (c) silanol condensation catalyst as a solution or dispersion liquid, etc. are mentioned. Especially, especially a method of of the above (a) and (b) is preferred. Quantity of a silanol condensation catalyst made to exist can be chosen in the range of 0.001 to 10 weight section to modified resin 100 weight section, and 0.01 to 5 weight section is preferred.

[0024] Before manufacturing a resin pipe by an extrusion method, other resin and various resin additives can be blended with raw material modified resin at the time of manufacturing a cross linked polyolefin pipe concerning this invention in the range which does not spoil the purpose of this invention. As other resin, low density polyethylene, medium density polyethylene, high density polyethylene, Straight-chain-shape low density polyethylene, an ethylene-vinylacetate copolymer, an ethylene-acrylic acid copolymer, ethylene propylene rubber, polypropylene, a propylene-butene-1 copolymer, propylene-hexene-1 copolymer, etc. are mentioned. Other resin is not limited to what was illustrated above. As a resin additive, colorant, a thermostabilizer, light stabilizer, an antioxidant, an ultraviolet ray absorbent, a rust-proofer, a bulking agent, fire retardant, etc. are mentioned.

[0025]. In order to make the above-mentioned modified resin construct a bridge under existence of a silanol condensation catalyst, after using as a pipe modified resin which blended a (i) silanol condensation catalyst by an extrusion method, put into water atmosphere. Or a pipe made of modified resin applied or impregnated with a (ii) silanol condensation catalyst can be twisted to methods, such as putting into water atmosphere. A bridge is constructed over a modified resin pipe by putting into this water atmosphere. Conditions at the time of putting into water atmosphere of a modified resin pipe are ordinary temperature -200 °C temperature requirements, and should just put a modified resin pipe in the range for 10 seconds - one week. Especially desirable conditions at the time of putting are ordinary temperature -130 °C temperature requirements, and ranges of them are 1 minute - 100 hours. the inside of this water atmosphere — putting — a process of passing a tank and cooling this modified resin pipe immediately after considering it as a pipe by an extrusion method — simultaneously, it can also carry out.

[0026] In order to have demonstrated intensity which continued and was excellent in a cross linked polyolefin pipe concerning this invention at a long period of time according to this invention persons' experiment, it turned out that it is required that a gel fraction (degree of cross linking) measured based on ISO 10147:1994 makes a bridge construct to not less than 65%. A degree of cross linking can be adjusted by changing a graft rate of a vinyl silane compound of modified resin, a kind of silanol condensation catalyst, quantity, conditions at the time of making a bridge construct (temperature, time), etc.

[0027]

[Example] Next, although this invention is explained still in detail based on an example, this invention is not limited to the following written examples, unless the meaning is exceeded.

[0028] [Example 1] It is a copolymer of the ethylene and alpha olefin which were manufactured using the single site catalyst. In MFR, density for 2.2g/10 minutes 0.898 g/cm³, Q value (Mw/Mn) Thing 100 weight section of 2.23, dicumyl peroxide 0.07 weight section, And weighing of the amount part of vinyltrimetoxysilane duplex was carried out, respectively, and it mixed with the

Henschel mixer, and by 26, with the single screw extruder of 40 m/mphi, ratio of length to diameter carried out melt kneading at the temperature of 210 **, carried out the graft of the silane compound, and obtained modified resin. MFRs of the obtained modified resin were 2.0g/10 minutes.

[0029]MFR blended with the modified resin 100 above-mentioned weight section five weight sections of masterbatches which density becomes from straight-chain-shape low-density-polyethylene 100 weight section of 0.924 g/cm³, and dibutyltin dilaurate 1 weight section for 0.9g/10 minutes. It equipped with the die of outer diameter 13m/mphi and thickness 1.5 m/m at the tip, ratio of length to diameter carried out melt kneading of this resin composition at the temperature of 200 ** with the full close-bladed-screw extrusion machine of 50 m/mphi of 24, and the resin pipe was extruded on condition of for extrusion rate/of 10 m. It was 25 (A) when the maximum load of the motor for screws of the extrusion machine in the middle of extrusion molding was measured for the resin pipe with the ampere meter. The extruded resin pipe is immersed in 80 ** warm water for 24 hours, was made to construct a bridge, and the cross linked polyolefin pipe was obtained. The audit observation of the surface appearance by a naked eye, a gel fraction (degree of cross linking), and the time to creep fracture were measured about the obtained cross linked polyolefin pipe. As for the gel fraction, the time to ISO 10147:1994 and creep fracture was based on ISO 1167:1996 (circumferential stress is 1.33MPa). A result is shown in table-1.

[0030][Example 2] It is a copolymer of the ethylene and alpha olefin which were manufactured using the single site catalyst, In MFR, density for 2.0g/10 minutes 0.918 g/cm³. Q value (Mw/Mn) Thing 100 weight section of 2.0, dicumyl peroxide 0.07 weight section. And weighing of the amount part of vinyltrimetoxysilane duplexs was carried out, respectively, and it mixed with the Henschel mixer, and by 26, with the single screw extruder of 40 m/mphi, ratio of length to diameter carried out melt kneading at the temperature of 210 **, carried out the graft of the silane compound, and obtained modified resin. MFRs of the obtained modified resin were 1.9g/10 minutes.

[0031]Five weight sections of masterbatches of the same kind were blended with having used it for the modified resin 100 above-mentioned weight section in Example 1, and the resin composition was obtained. The resin pipe was extruded [in / for this resin composition / Example 1] in the same procedure. While having extruded the resin pipe, surface appearance, a gel fraction (degree of cross linking), the time to creep fracture, etc. were similarly measured in Example 1 about the maximum load of the motor for screws of an extrusion machine, and the obtained cross linked polyolefin pipe. A result is shown in table-1.

[0032][Example 3] to using-in Example 2-it, of the same kind ethylene, and alpha olefin 100 weight section. Dicumyl peroxide 0.075 weight section, the amount part of vinyltrimetoxysilane duplexs, And also in Example 1, the pipe was extruded on the same conditions with the extrusion machine which blended dibutyltin dilaurate 0.05 weight section, was mixed with the Henschel mixer, and uses this mixture for resin pipe manufacture in Example 1. In Example 1, surface appearance, a gel fraction (degree of cross linking), the time to creep fracture, etc. were similarly measured about the maximum load of the motor for screws of an extrusion machine, and the obtained cross linked polyolefin pipe. A result is shown in table-1.

[0033][Comparative example 1] Straight-chain-shape low-density-polyethylene (MFR 2.1g/10 minutes, In density, 0.920 g/cm³ and Q value (Mw/Mn) to 3.5) 100 weight section. Weighing of dicumyl peroxide 0.07 weight section and the amount part of vinyltrimetoxysilane duplexs was carried out, respectively, and it mixed with the Henschel mixer, and by 26, with the single screw extruder of 40 m/mphi, ratio of length to diameter carried out melt kneading at the temperature of 210 **, carried out the graft of the silane compound, and obtained modified resin. MFRs of the obtained modified resin were 0.15g/10 minutes. Also in Example 1, the pipe was extruded on the same conditions with the extrusion machine which blended five weight sections of masterbatches of dibutyltin dilaurate of the same kind with having used it in Example 1, was mixed to this modified resin with the Henschel mixer, and uses this mixture for it for resin pipe manufacture in Example 1. In Example 1, surface appearance, a gel fraction (degree of cross

linking), the time to creep fracture, etc. were similarly measured about the resin pipe which was able to obtain the maximum load of the motor for screws of an extrusion machine. A result is shown in table-1.

[0034]

[Table 1]

表-1

項目 \ 番号	実施例1	実施例2	実施例3	比較例1
変性樹脂のMFR(g/10分)	2.0	1.9	-	0.15
モーターの最大負荷 (A)	25	25	25	32
樹脂管の表面状態	極めて良好	極めて良好	極めて良好	表面に小さいブツ多数
ゲル分率 (重量%) (%)		80	79	74
クリープ破壊までの時間(hrs)	>10000	>10000	>10000	8700

[0035]The following thing becomes clear from table-1.

- (1) As for the cross linked polyolefin pipe concerning this invention, the motor load of a making machine does not become large at the time of manufacture.
- (2) The cross linked polyolefin pipe concerning this invention has the long time to creep fracture.

- (3) The resin pipe of a comparative example has the short time to creep fracture to this, and the motor load of the making machine at the time of manufacture is also large.

[0036]

[Effect of the Invention]This invention is as having explained to details above.

Doing the following specially outstanding effects so, the industrial utility value is size very much.

1. Since the load of a making machine does not become large at the time of cross linked polyolefin pipe manufacture, the large-scale making machine of the cross linked polyolefin pipe concerning this invention is unnecessary, and it can be manufactured with the conventional making machine.
2. Since it is not necessary to make the cross linked polyolefin pipe concerning this invention into an elevated temperature at the time of manufacture, a glow does not generate it in the modified resin constituent of a raw material.
3. Since the cross linked polyolefin pipe concerning this invention uses the narrow polyolefin copolymer of molecular weight distribution as a raw material and makes the degree of cross linking high, it can continue at a long period of time, and can maintain the especially outstanding creep performance.

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TECHNICAL FIELD

[Field of the Invention]This invention relates to a cross linked polyolefin pipe. It is related with the outstanding endurance and the cross linked polyolefin pipe which demonstrates creep performance over a long period of time, and is especially used as the conduit tube, the protective tube of the cable for communication, a gas pipe, feed water and a hot-water pipe, a lead pipe of the heating fluid of a floor heater, etc. in more detail.

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PRIOR ART

[Description of the Prior Art]It is common knowledge to improve physical properties, such as heat resistance, creep resistance, environmental-stress-cracking-resistance nature (ESC), and chemical resistance, by making polyethylene construct a bridge conventionally. In order to continue at a long period of time and to demonstrate the creep performance outstanding with these cross-linked polyethylene pipe, it is made good for a melt flow rate (MFR) to use the resin which carried out the graft of the vinylsilane to low namely, polyethylene with a large molecular weight, and denaturalized.

[0003]However, probably in order for the chains of an ultrahigh-molecular-weight portion to construct a bridge in the modified resin having contained the polyethylene molecule with a large molecular weight, the motor load of a making machine becomes large at the time of cross-linked polyethylene pipe manufacture, and as a result, power consumption becomes large, and it becomes a high cost, and is not desirable. Although there is a method of making melting temperature of modified resin high and manufacturing a pipe as a method of on the other hand preventing the motor load of a making machine from becoming large, since this method promotes generating of a glow of modified resin and reduces the value as the long-term creep performance and the product of a pipe, it is not preferred.

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EFFECT OF THE INVENTION

[Effect of the Invention]This invention is as having explained to details above.
Doing the following specially outstanding effects so, the Industrial utility value is size very much.

1. Since the load of a making machine does not become large at the time of cross linked polyolefin pipe manufacture, the large-scale making machine of the cross linked polyolefin pipe concerning this invention is unnecessary, and it can be manufactured with the conventional making machine.
2. Since it is not necessary to make the cross linked polyolefin pipe concerning this invention into an elevated temperature at the time of manufacture, a glow does not generate it in the modified resin constituent of a raw material.
3. Since the cross linked polyolefin pipe concerning this invention uses the narrow polyolefin copolymer of molecular weight distribution as a raw material and makes the degree of cross linking high, it can continue at a long period of time, and can maintain the especially outstanding creep performance.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]As a result of repeating research wholeheartedly in view of the above-mentioned situation, this invention persons vinylsilane as a graft and a raw material to denature. The motor load of the making machine at the time of manufacture does not become large, but the cross linked polyolefin pipe which selected the copolymer of specific ethylene and alpha olefins and was made to construct a bridge by a specific method comes to complete this invention based on the knowledge which continues at a long period of time and maintains the creep performance outstanding moreover.

[0005]The purpose of this invention is as follows. 1. Provide the cross linked polyolefin pipe with which the motor load of a making machine does not become large at the time of manufacture. 2. Provide the cross linked polyolefin pipe which does not produce generating of a glow of raw resin at the time of manufacture. 3. Provide the cross linked polyolefin pipe which continues at a long period of time and maintains the outstanding creep performance.

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MEANS

[Means for Solving the Problem] In a cross linked polyolefin pipe which consists of a copolymer of ethylene and alpha olefin whose carbon number is four or more in this invention in order to solve an aforementioned problem, In a melt flow rate, density for 0.1-95g/10 minutes 0.850 - 0.970 g/cm³, [this copolymer] Q value (Mw/Mn) is less than 3.0, and carry out the graft of the vinyl silane compound to this copolymer under existence of a radical generator, and it is considered as modified resin. This modified resin is put into water atmosphere under existence of a silanol condensation catalyst, and a cross linked polyolefin pipe making not less than 65% of a gel fraction construct a bridge is provided.

[0007] In a cross linked polyolefin pipe which consists of a copolymer of ethylene and alpha olefin whose carbon number is four or more further in this invention, In a melt flow rate, density for 0.1-95g/10 minutes 0.850 - 0.970 g/cm³, [this copolymer] A process of Q value (Mw/Mn) being less than 3.0, and making a vinyl silane compound this copolymer with modified resin under existence of a radical generator, A silanol condensation catalyst is added with a single making machine, dew is carried out into water atmosphere after that, and a cross linked polyolefin pipe making not less than 65% of a gel fraction construct a bridge is provided.

[0008]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. In this invention, the polyolefine refers to the copolymer of ethylene and the alpha olefins whose carbon number is four or more. As alpha olefins whose carbon number is four or more, 1-butene, a 2-methyl-1-butene, 1-pentene, 2-methyl-1-pentene, 1-hexene, a 2,2-dimethyl-1-butene, a 2-methyl-1-hexene, 4-methyl-1-pentene, 1-heptene, a 2-methyl-1-hexene, A 3-methyl-1-hexene, 2,2-dimethyl-1-pentene, 3,3-dimethyl-1-pentene, 2,3-dimethyl-1-pentene, 3-ethyl-1-pentene, a 2,2,3-trimethyl-1-butene, 1-octene, 2,2,4-trimethyl-1-octene, etc. are mentioned.

[0009] The above-mentioned copolymer can be manufactured using a metallocene catalyst. Generally the designation of the catalyst of the structure which sandwiched the unsaturated compound of a pi electron system for the transition metal is carried out, the structure is indicated in the international publication W091 No. -04257 gazette, and bis(cyclopentadienyl) metallic compounds of a metallocene catalyst are typical. As a metallocene catalyst, the compound in which 1, two or more cyclopentadienyl rings, or the analog of those exists in tetravalent transition metals, such as titanium, a zirconium, nickel, palladium, hafnium, and platinum, as ligand (ligand) is specifically mentioned.

[0010] The metallocene catalyst which can be preferably used for manufacture of the above-mentioned copolymer is a nonelectrolyte complex, two cyclopentadienyl rings have regular pentagon structure, and faces in parallel mutually, and presents the spacial configuration which a metal atom is inserted in the middle and consists of a molecule of sandwich structure. The ethylene and alpha olefin of a raw material of a copolymer, Since it cannot contact, but metal and a monomer will always contact from a fixed direction and stereospecific polymerization happens from the direction blocked in three dimensions by the substituent combined with the five membered ring combined with the metal atom, A molecular weight, branching structure, and a crystal structure become fixed, and the olefin system copolymer which a catalyst is called a single site catalyst and obtained has them. [preferred]

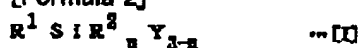
[0011]Restriction in particular does not have a manufacturing method of the above-mentioned copolymer, and it is good in both a solution polymerization method gas phase polymerization process a suspension polymerization method a mass polymerization method, etc.

[0012]In order to obtain the cross linked polyolefin pipe concerning this invention according to this invention persons' experiment, the melt flow rate (MFR) which measured the above-mentioned copolymer based on JIS K6922-2 The conditions of the temperature of 190 ** and 2.16 kg of load 0.1-95g/range for 10 minutes, The density measured based on JIS K6922-2 was found by being the range of 0.850-0.970g/cm³, and that molecular-weight-distribution Q value {weight-average-molecular-weight (Mw) / number average molecular weight (Mn)} is [less than 3.0 thing] further suitable.

[0013]The cross linked polyolefin pipe concerning this invention carries out the graft of the vinyl silane compound to the above-mentioned olefine copolymer under existence of a radical generator, is used as modified resin, and makes this modified resin construct a bridge under existence of a silanol condensation catalyst. As a vinyl silane compound, what is expressed with the following general formula [I] is mentioned.

[0014]

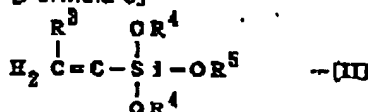
[Formula 2]



[0015]In general formula [I], R¹ is an ethylene nature unsaturation hydrocarbon group or a hydrocarbon oxy group, and has radical reactivity. As an example of such a basis, a vinyl group, an allyl group, a butenyl group, gamma-(meta) acryloxypropyl group, etc. are mentioned. R² is an aliphatic series saturation hydrocarbon group, and a methyl group, an ethyl group, a propyl group, a decyl group, etc. are mentioned as an example. Y expresses the organic group which can be hydrolyzed and a methoxy group, an ethoxy basis, a formyloxy group, an acetoxy group, a propionyloxy group, an arylamino group, etc. are mentioned as an example. n is 0, 1, or 2. Especially a desirable thing is a compound expressed with the following general formula [II] especially.

[0016]

[Formula 3]



[0017]As for R³, in general formula [II], a with a carbon number of four or less straight chain or a branched alkyl group, and R⁵ of H or CH₃, and R⁴ are a with a carbon number of four or less straight chain, a branched alkyl group, or a phenyl group. Specifically, vinyltrimetoxysilane, vinyltriethoxysilane, a vinyl tripropoxy silane, etc. are mentioned.

[0018]When denaturing an olefine copolymer, the quantity of the vinyl silane compound made to exist in the system of reaction to denature is determined by the degree of cross linking of the resin pipe made into the purpose, the reaction condition (temperature, time), etc., but. It is chosen from a viewpoint of economical efficiency and the ease of the handling under reaction front and reaction in the range of 0.1 to 15 weight section to polyolefin copolymer 100 weight section. If there is too little this quantity, a graft rate will be low and sufficient degree of cross linking will not be obtained. If too large, the resin pipe of mold goods may serve as an appearance defect under the influence of a conversely unreacted vinyl silane compound, etc., and it is not desirable. The range with a preferred quantity of a vinyl silane compound is 0.3 to 10 weight section, and especially a desirable thing is 0.5 to 7 weight section.

[0019]As for a radical generator, it is preferred to choose from compounds which can generate an uncombined radical and have the half-life for less than 6 minutes at grafting reaction temperature under grafting reaction conditions. A compound which has the half-life for less than

1 minute at grafting reaction temperature is more preferred. All compounds indicated to JP,48-1711,B can use these radical generators. Specifically, azo compounds, such as organic peroxide, such as benzoyl peroxide, dicumyl peroxide, di-*t*-butyl peroxide, and *t*-butoxy 2-ethylhexanoate, azobisisobutyronitrile, and methyl azobisisobutyrate, are mentioned.

[0020]When carrying out the grafting reaction of the vinyl silane compound to an olefine copolymer, quantity of a radical generator made to exist in a grafting reaction system is chosen in the range of 0.001 to 5 weight section to olefine copolymer 100 weight section. If there are too many amounts of grafts of a vinyl silane compound conversely few when there is too little quantity of a radical generator made to exist, crosslinking reaction which is not made into the purpose depended on a radical generator may advance, and it may become causes, such as aggravation etc. of appearance of a resin pipe which are the poor flowing characteristic and mold goods, and is not desirable. It is the range of 0.01 to 2.0 weight section more preferably.

[0021]A method of making carry out the graft of the vinyl silane compound to an olefine copolymer, and using as modified resin can be based on a method indicated in publications, such as JP,48-1711,B, JP,59-36115,A, and JP,55-9611,A, and can be manufactured easily.

[0022]In order to obtain a cross linked polyolefin pipe concerning this invention, the above-mentioned modified resin is made to construct a bridge under existence of a silanol condensation catalyst. As a silanol condensation catalyst, metal carboxylate, such as tin, zinc, iron, lead, and cobalt, titanate and an organic metallic compound of chelate compound, an organic base, inorganic acid, organic acid, etc. are mentioned. Specifically Dibutyltin dilaurate, dibutyltin diacetate, a dioctyl tin JIRAU rate, The first tin of acetic acid, the first tin of caprylic acid, lead naphthenate, cobalt naphthenate, tetrabutyl titanate ester, titanate acid tetranonyl ester, dibutyl amine, hexylamine, pyridine, sulfuric acid, chloride, toluenesulfonic acid, acetic acid, stearic acid, maleic acid, etc. are mentioned.

[0023]When making said modified resin construct a bridge, in order to make a silanol condensation catalyst exist in a crosslinking reaction system, (a) How to blend as a masterbatch which carried out melt kneading of the silanol condensation catalyst to polyolefine a priori, (b) A method of blending a silanol condensation catalyst with modified resin directly as it is at the time of manufacture, a method of applying or impregnating with a pipe made of modified resin by using the (c) silanol condensation catalyst as a solution or dispersion liquid, etc. are mentioned. Especially, especially a method of of the above (a) and (b) is preferred. Quantity of a silanol condensation catalyst made to exist can be chosen in the range of 0.001 to 10 weight section to modified resin 100 weight section, and 0.01 to 5 weight section is preferred.

[0024]Before manufacturing a resin pipe by an extrusion method, other resin and various resin additives can be blended with raw material modified resin at the time of manufacturing a cross linked polyolefin pipe concerning this invention in the range which does not spoil the purpose of this invention. As other resin, low density polyethylene, medium density polyethylene, high density polyethylene, Straight-chain-shape low density polyethylene, an ethylene-vinylacetate copolymer, an ethylene-acrylic acid copolymer, ethylene propylene rubber, polypropylene, a propylene-butene-1 copolymer, propylene-hexene-1 copolymer, etc. are mentioned. Other resin is not limited to what was illustrated above. As a resin additive, colorant, a thermostabilizer, light stabilizer, an antioxidant, an ultraviolet ray absorbent, a rust-proofer, a bulking agent, fire retardant, etc. are mentioned.

[0025]. In order to make the above-mentioned modified resin construct a bridge under existence of a silanol condensation catalyst, after using as a pipe modified resin which blended a (i) silanol condensation catalyst by an extrusion method, put into water atmosphere. Or a pipe made of modified resin applied or impregnated with a (ii) silanol condensation catalyst can be twisted to methods, such as putting into water atmosphere. A bridge is constructed over a modified resin pipe by putting into this water atmosphere. Conditions at the time of putting into water atmosphere of a modified resin pipe are ordinary temperature -200 °C temperature requirements, and should just put a modified resin pipe in the range for 10 seconds - one week. Especially desirable conditions at the time of putting are ordinary temperature -130 °C temperature requirements, and ranges of them are 1 minute - 100 hours, the inside of this water atmosphere — putting — a process of passing a tank and cooling this modified resin pipe immediately after.

considering it as a pipe by an extrusion method — simultaneously, it can also carry out.
[0026] In order to have demonstrated intensity which continued and was excellent in a cross
linked polyolefin pipe concerning this invention at a long period of time according to this
invention persons' experiment, it turned out that it is required that a gel fraction (degree of
cross linking) measured based on ISO 10147:1994 makes a bridge construct to not less than 65%.
A degree of cross linking can be adjusted by changing a graft rate of a vinyl silane compound of
modified resin, a kind of silanol condensation catalyst, quantity, conditions at the time of making
a bridge construct (temperature, time), etc.

[Translation done.]

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.*** shows the word which can not be translated.

3.In the drawings, any words are not translated.

EXAMPLE

[Example]Next, although this invention is explained still in detail based on an example, this invention is not limited to the following written examples, unless the meaning is exceeded.

[0028][Example 1] It is a copolymer of the ethylene and alpha olefin which were manufactured using the single site catalyst. In MFR, density for 2.2g/10 minutes 0.898 g/cm³, Q value (Mw/Mn) Thing 100 weight section of 2.23, dicumyl peroxide 0.07 weight section, And weighing of the amount part of vinyltrimetoxysilane duplexs was carried out, respectively, and it mixed with the Henschel mixer, and by 26, with the single screw extruder of 40 m/mphi, ratio of length to diameter carried out melt kneading at the temperature of 210 **, carried out the graft of the silane compound, and obtained modified resin. MFRs of the obtained modified resin were 2.0g/10 minutes,

[0029]MFR blended with the modified resin 100 above-mentioned weight section five weight sections of masterbatches which density becomes from straight-chain-shape low-density-polyethylene 100 weight section of 0.924 g/cm³, and dibutyltin dilaurate 1 weight section for 0.9g/10 minutes. It equipped with the die of outer diameter 13m/mphi and thickness 1.5 m/m at the tip, ratio of length to diameter carried out melt kneading of this resin composition at the temperature of 200 ** with the full close-bladed-screw extrusion machine of 50 m/mphi of 24, and the resin pipe was extruded on condition of for extrusion rate/of 10 m. It was 25 (A) when the maximum load of the motor for screws of the extrusion machine in the middle of extrusion molding was measured for the resin pipe with the ampere meter. The extruded resin pipe is immersed in 80 ** warm water for 24 hours, was made to construct a bridge, and the cross linked polyolefin pipe was obtained. The audit observation of the surface appearance by a naked eye, a gel fraction (degree of cross linking), and the time to creep fracture were measured about the obtained cross linked polyolefin pipe. As for the gel fraction, the time to ISO 10147:1994 and creep fracture was based on ISO 1167:1996 (circumferential stress is 1.33MPa). A result is shown in table-1.

[0030][Example 2] It is a copolymer of the ethylene and alpha olefin which were manufactured using the single site catalyst. In MFR, density for 2.0g/10 minutes 0.918 g/cm³, Q value (Mw/Mn) Thing 100 weight section of 2.0, dicumyl peroxide 0.07 weight section, And weighing of the amount part of vinyltrimetoxysilane duplexs was carried out, respectively, and it mixed with the Henschel mixer, and by 26, with the single screw extruder of 40 m/[m] phi, ratio of length to diameter carried out melt kneading at the temperature of 210 **, carried out the graft of the silane compound, and obtained modified resin. MFRs of the obtained modified resin were 1.9g/10 minutes,

[0031]Five weight sections of masterbatches of the same kind were blended with having used it for the modified resin 100 above-mentioned weight section in Example 1, and the resin composition was obtained. The resin pipe was extruded [in / for this resin composition / Example 1] in the same procedure. While having extruded the resin pipe, surface appearance, a gel fraction (degree of cross linking), the time to creep fracture, etc. were similarly measured in Example 1 about the maximum load of the motor for screws of an extrusion machine, and the obtained cross linked polyolefin pipe. A result is shown in table-1.

[0032][Example 3] to using in Example 2-it, of the same kind ethylene, and alpha olefin 100 weight section. Dicumyl peroxide 0.075 weight section, the amount part of vinyltrimetoxysilane duplexs, And also in Example 1, the pipe was extruded on the same conditions with the extrusion machine which blended dibutyltin dilaurate 0.05 weight section, was mixed with the Henschel mixer, and uses this mixture for resin pipe manufacture in Example 1. In Example 1, surface appearance, a gel fraction (degree of cross linking), the time to creep fracture, etc. were similarly measured about the maximum load of the motor for screws of an extrusion machine, and the obtained cross linked polyolefin pipe. A result is shown in table-1.

[0033][Comparative example 1] Straight-chain-shape low-density-polyethylene (MFR 2.1g/10 minutes, In density, 0.920 g/cm³ and Q value (Mw/Mn) to 3.5) 100 weight section. Weighing of dicumyl peroxide 0.07 weight section and the amount part of vinyltrimetoxysilane duplexs was carried out, respectively, and it mixed with the Henschel mixer, and by 26, with the single screw extruder of 40 m[m] phi, ratio of length to diameter carried out melt kneading at the temperature of 210 **, carried out the graft of the silane compound, and obtained modified resin, MFRs of the obtained modified resin were 0.15g/10 minutes. Also in Example 1, the pipe was extruded on the same conditions with the extrusion machine which blended five weight sections of masterbatches of dibutyltin dilaurate of the same kind with having used it in Example 1, was mixed to this modified resin with the Henschel mixer, and uses this mixture for it for resin pipe manufacture in Example 1. In Example 1, surface appearance, a gel fraction (degree of cross linking), the time to creep fracture, etc. were similarly measured about the resin pipe which was able to obtain the maximum load of the motor for screws of an extrusion machine. A result is shown in table-1.

[0034]

[Table 1]

表-1

項目 \ 番号	実施例1	実施例2	実施例3	比較例1
粘性樹脂のMFR(g/10分)	2.0	1.9	—	0.15
モーターの最大負荷 (A)	25	25	25	32
樹脂管の表面状態	極めて良好	極めて良好	極めて良好	表面に小さい ブツ多数
ゲル分率 (架橋度) (%)		80	79	74
クリープ破壊までの時間(Hrs)	>10000	>10000	>10000	8700

[0035]The following thing becomes clear from table-1.

- (1) As for the cross linked polyolefin pipe concerning this invention, the motor load of a making machine does not become large at the time of manufacture.
- (2) The cross linked polyolefin pipe concerning this invention has the long time to creep fracture.
- (3) The resin pipe of a comparative example has the short time to creep fracture to this, and the motor load of the making machine at the time of manufacture is also large.

[Translation done.]